

Quarterly Progress Report on  
Standard Agreement No. 04-329  
For the Period  
November 1, 2005 through February 28, 2006

***Development of an Improved VOC Analysis Method for Architectural Coatings***

Prepared for California Air Resources Board  
and the California Environmental Protection Agency

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### **Disclaimer-**

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## **Acknowledgements**

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## **I. Work This Reporting Period**

This report summarizes work performed on the project from November 1, 2005 through February 28, 2006.

### **A. Task I Activities and Methods Development Summary**

During this time period, work continued on Task 1 activities

- Sources of error in current methods
- Comparison of existing methods
- Develop confidence limits calculation methods
- Determine confidence limits for coatings in ARB 2001 survey
- Consult on development of methods manual
- Purchase and begin installation and testing of GC/MS/FID system

Progress was made on all activities and work is continuing toward completion of Task 1. All Task I activities will be completed on schedule. Installation of the remaining part of our new chromatography system, the static headspace analyzer, was completed early during this reporting period and we concentrated our efforts on further testing of the full GC/MS/FID/static headspace system. Since the core purpose of this project is development of a comprehensive test method, we felt it imperative we become familiar with all features of this system as soon as possible. In addition we have begun experimental research on new VOC analysis techniques to be included in the final method. This work is proceeding very well. Our plan is to have these methods developed to the point where we can use them for testing the samples chosen by ARB during the coming summer. This report details our work on testing the new system and methods development. The work is described under the following headings: headspace analysis, modification of ASTM Method 6886 using water as dilution solvent, initial studies with two component coatings.

The new GC/MS/FID system, including a static headspace analyzer has now been installed and has been tested with several coatings. For another related but independent project, we analyzed twenty-eight coatings as part of an NPCA/SCAQMD Rule 1113 assessment using our older GC system. As part of the work for this reporting period, several of these coatings have been analyzed with the new system in order to test its capabilities and to familiarize ourselves with its operation and the results are compared with those obtained using ASTM Method 6886 on our older GC system. The new static headspace system gives excellent results for the speciated VOC content of the waterborne coatings we have analyzed. We have developed and tested a modification of Method 6886 in which water is used as the solvent for analyzing coatings instead of tetrahydrofuran. The use of static headspace also shows promise for the analysis of two-component systems and appears to give VOC content results which are nearly the same as those expected by EPA's Method 24 for total volatile content (ASTM Method 2369).

### **B. Headspace Analysis**

The static headspace analyzer (Agilent Model G1888 Headspace Sampler) consists of an autosampler capable of holding 70 samples, programmable oven with capacity for twelve

samples, automated pressurizing and injector for obtaining headspace sample with capability for multiple headspace extraction modes, and inert heated transfer line. The sampler is shown below in Figure 1.

Figure 1 Agilent Model G1888 Static Headspace Sampler



Samples are placed in 22 mL headspace vials and sealed with a special crimper. Samples can be equilibrated for any specified time at temperatures from 40°C to 230°C. This is especially important for VOC analysis where equilibration temperature can be adjusted to match particular conditions in traditional VOC analyses, for example 110°C as used in EPA Method 24. The equilibration temperature could also be adjusted to match a specified cure temperature for a two-component coatings system. Multiple samples can be obtained from a given sample, if desired. The sample is automatically transferred from the heated sample loop to the GC inlet through a heated, inert transfer line insuring all the sample reaches in inlet at the same time.

### C. Modification of ASTM Method 6886 using Water as Dilution Solvent

ASTM Method 6886 is a direct injection gas chromatographic method for analysis of low VOC water-based coatings developed at Cal Poly, San Luis Obispo. We have modified this method by substituting water containing an internal standard (ethoxyethanol) for the tetrahydrofuran used to dilute the paint sample. Sample preparation methods for both static headspace analysis and direct injection into a gas chromatograph are given below.

#### Sample Preparation

1. Static Headspace Analysis: 1.5 to 2 grams of the well-mixed coating, weighed to 0.1 mg is added to a 40mL vial containing ca. 5g of ceramic beads. 10.0 mL of water containing 0.2% ethoxyethanol (EE) internal standard is added. The vial is capped with a Teflon-lined cap and mixed by shaking for 2 minutes. A small quantity of surfactant (Triton X-100) may be added if desired to aid in dispersion of the sample but is generally not required since most waterborne coatings already contain surfactant and since most VOC components in waterborne coatings are water soluble. Five (5) microliters of the dispersion are transferred to a 22mL headspace vial and sealed with a crimp cap. Figure 2 shows the sample preparation procedure in which 20mL vials were used.
2. Direct Injection Analysis: The dispersion in 1 is diluted with 10 mL of acetone or other suitable solvent. The contents are mixed by shaking.

Figure 2. Headspace sample preparation showing vial with ceramic beads, vial with beads and paint sample dispersed in water containing internal standard, and 5  $\mu$ L sample in headspace vial



ceramic beads

dispersed sample

headspace  
sample

### Gas Chromatographic Analysis

- A. Static Headspace Analysis: The headspace vial containing 5 $\mu$ L of coating dispersion is placed in the headspace analyzer (Agilent Model G1888 Headspace Sampler). The sample is equilibrated at 110°C for 20 minutes. After equilibration, one (1) mL of the headspace is transferred to the gas chromatograph (sample loop and transfer line temperature = 160°C). GC conditions are as follows:

Column: 30m x 0.25mm DB-5 (film thickness =1.0 $\mu$ m) or equivalent

Detector: flame ionization detector (FID) at 270°C

Inlet Temp: 250°C

Split Ratio: 100:1

Temperature program: Initial Time 4 min; Ramp 20°C per min to 260°C; hold 10 min.

- B. Direct Injection: One (1)  $\mu$ L of the dispersion diluted with acetone or other suitable solvent is injected directly into the GC inlet. The GC analysis conditions are the same as they are for the headspace conditions described in A above.

### Results

We have compared results from ASTM 6886 on three water-based architectural coatings: a gloss acrylic latex coating with a reported coating VOC of 142 g/L (Coatings A), a zero-VOC interior eggshell enamel which we spiked with known amounts of Texanol (Coating B), and an interior/exterior sealer/primer with a reported coating VOC of 142 g/L (Coatings C).

Coating A: PPG Pittsburgh Paints, Manor Hall I/E Gloss Acrylic Latex 52-110 Series White and Pastel Base. This coating was first analyzed by us in September, 2005 for the NPCA/SCAQMD Rule 1113 assessment using ASTM Method 6886 as it appears in the current ASTM literature with THF as the dispersion solvent and p-cymene as internal standard. The chromatogram for this run is shown in Figure 3. The same coating was then analyzed using both direct injection and static headspace with water as the dispersing solvent. Chromatograms for these runs are shown in Figures 4 and 5. Numerical results for the three separate analyses are shown in Table 1.

Figure 3. Direct Injection FID Chromatogram of Coating A in THF with p-Cymene as Internal Standard (Current ASTM Method D6886)

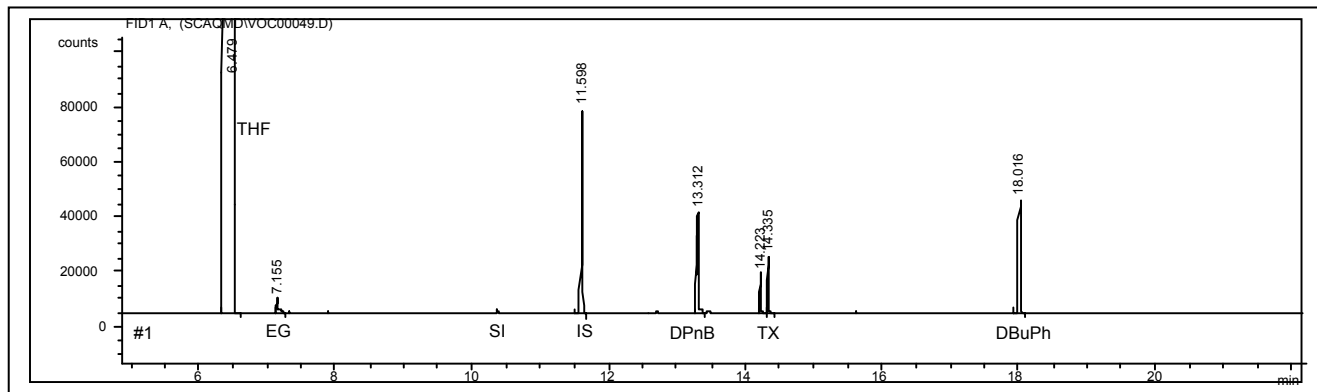


Figure 4. Direct Injection FID Chromatogram of Coating A in Water with Ethoxyethanol as Internal Standard (Modified ASTM Method D6886)

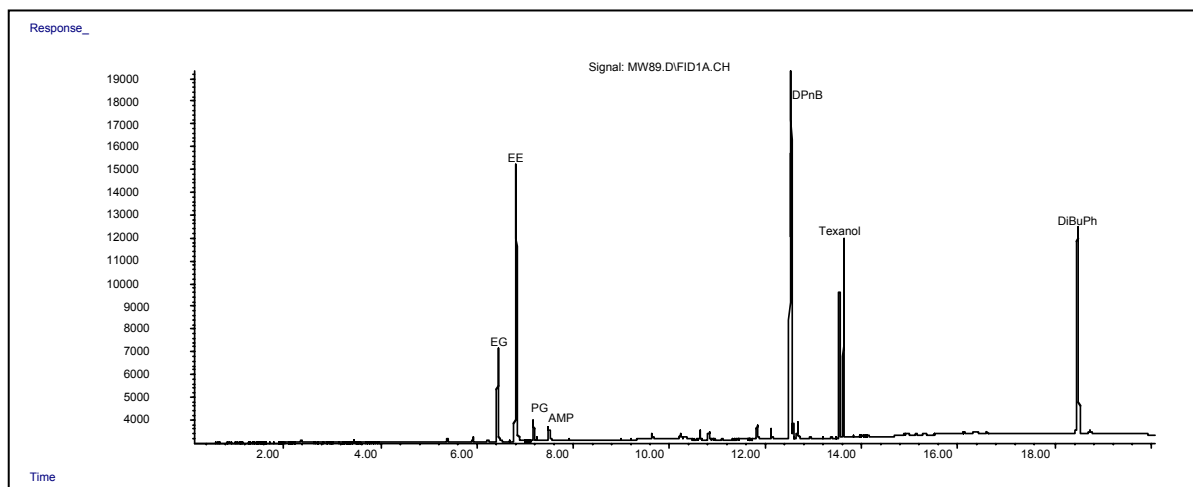


Figure 5. Static Headspace Injection FID Chromatogram of Coating A in Water with Ethoxyethanol as Internal Standard (Modified ASTM Method D6886)

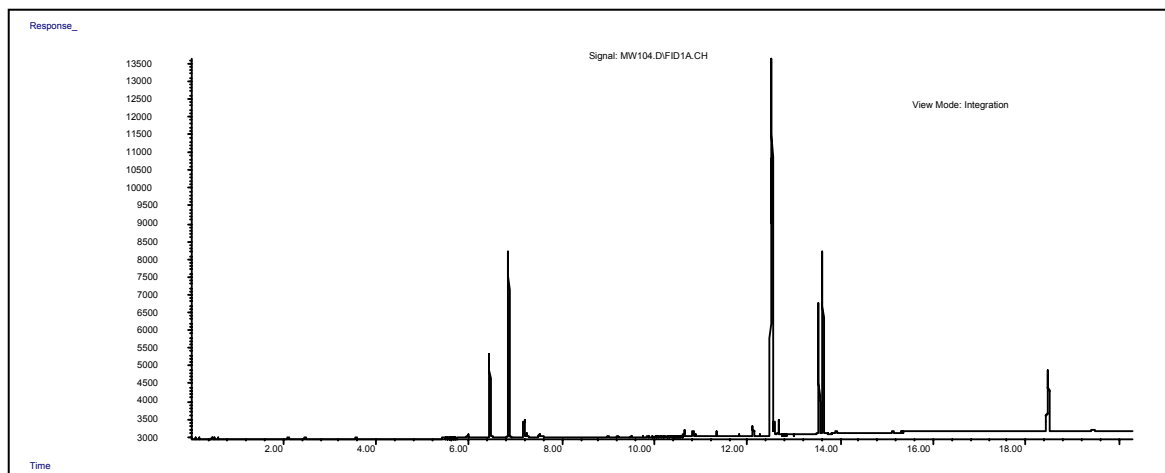




Table 1. Speciated Results for Coating A Using Direct Injection by the Standard D6886 Method, Modified D6886 Method and Static Headspace D6886 Method

Cpd	THF, Direct	Water, Direct	Water, Headspace	Contribution to Coating VOC, Direct Methods
Ethylene glycol	0.82%	1.00%	0.91%	24 to 30
Propylene glycol	ND	0.15%	0.12%	0 to 5
AMP-95	ND	0.12%	0.04%	0 to 4
Dipropylene glycol, monobutyl ether	2.23%	2.44%	2.39%	66 to 72
Texanol	1.04%	1.05%	1.03%	31 to 32
Dibutyl phthalate	1.36%	1.27%	0.62%	???
Total	5.45%	6.04%	4.99%	124 to 145*
* Dibutyl phthalate not used to calculate Coating VOC				

% Texanol lost during D2369 volatiles determination	76 -88
% Dibutyl phthalate lost during D2369 volatiles determination	43 - 50
Calculated water, wt %	45.67
REPORTED VALUE, Coating VOC	142

## Discussion

Direct injection determination of VOCs by Method D6886 shows all of the volatile organic components present in a coating. Using this methodology, the sample to be analyzed is injected into the hot inlet of a gas chromatograph, generally operated near 250°C. This inlet temperature results in vaporization of all of the volatile components. The current EPA 24 method for VOC determination defines a VOC as that portion of the volatile organic components that evaporate from a sample during one hour at 110°C. For the coating described here (coating A), US paint manufacturers generally classify Texanol (boiling point = 254°C) as a VOC and dibutyl phthalate (boiling point = 350°C) as a non-VOC. In determining the total VOC content by Method 24, laboratories generally use ASTM Method D2369, Test Method for Volatile Content of Coatings, in which a specified amount of sample is heated for one hour at 110°C. The amount of sample used for coatings with a solids content below 50% is  $0.5 \pm 0.1$  grams. The sample is dispersed prior to heating with  $3.0 \pm 1.0$  grams of water and is then heated at  $110 \pm 5^\circ\text{C}$  for one hour. These conditions generally give results which are within the published precision of D2369 but do not give information about the nature of the VOCs which evaporate during the determination. We performed GC analysis on samples extracted from dried paint films to determine the amount of specific compounds still remaining in the films after heating for one hour at 110°C. Results show that the D2369 conditions can give a range of semi-volatile component evaporation of 76 to 88% for Texanol and 43 to 50% for dibutyl phthalate. Lower evaporation amounts result from maximizing the sample amount (i.e., 0.6g instead of 0.5g) and minimizing the water dispersant (i.e., 2.0g instead of 3.0g). The opposite is true when the sample amount is minimized and water dispersant is maximized.

Our static headspace analysis of coating A indicates that dibutyl phthalate is in fact a VOC under D2369 weight loss conditions. The static headspace temperature equilibration of the sample is the same as for D2369 determination (110°C) though the time at this temperature is shorter (20 minutes by headspace and 60 minutes by D2369). Results obtained for dibutyl phthalate by static headspace indicate that approximately the same amount is vaporized as by D2369 (ca. 50% in each case – see Table 1).

In Europe, ISO regulations specify the VOC content of waterborne coatings to be determined by gas chromatography. Specifically, *ISO 11890-2, Paints and varnishes – Determination of volatile organic compound (VOC) content – Part 2: Gas-chromatographic method*, uses a VOC upper boiling point limit of 250°C and this limit is defined chromatographically by the retention time of diethyl adipate on a 60m poly(6% cyanopropylphenyl/94% dimethylsiloxane) (DB-1301™) capillary column. This approach greatly simplifies the gas chromatographic determination of VOC content in that the EPA 24 (ASTM D2369) definitions of VOC no longer apply. It is our opinion that Texanol would be the perfect boiling point marker since it is present in many waterborne architectural coatings and is easily identified by its unique two-peak chromatographic signal. Making the boiling point cut-off after elution of Texanol (i.e., counting Texanol as a VOC) would make the method approximately equivalent to weight loss by D2369. In Europe Texanol is not considered a VOC because the chosen boiling point marker (diethyl adipate) elutes ahead of Texanol on the capillary column specified in the ISO method.

Coating B: Benjamin Moore, Eco Spec Interior Latex Eggshell Enamel Pastel Base 223 1B

This coating contained no VOC's when analyzed by the unmodified ASTM D6886 method using THF as analysis solvent. In order to test the accuracy of the modified D6886 method and the static headspace method using water as dispersant, this coating was spiked with a known quantity of Texanol (1.74% by weight) and then analyzed by the two new methods. The results of this study are given below in Table 2.

Table 2. Analysis of Zero VOC Latex Eggshell Enamel by ASTM D6886 and analysis of same paint spiked with 1.74% Texanol by modified D6886 using direct and static headspace methods

Texanol	Method	Experimental VOC Content, Wt %
No Spike	Unmodified Direct D6886	0
1.74% Spike	Modified Direct D6886	1.81
1.74% Spike	Static Headspace	1.79

Coating C: Masterchem, KILZ Premium, Sealer-Primer-Stainblocker I/E

This coating contained several VOCs and was analyzed using ASTM D6886 (THF, Direct), modified D6886 by direct injection (Water, Direct) and modified D6886 by static headspace (Water, Headspace). Results are shown below in Table 3 along with the calculated percent Texanol lost during volatiles determination using ASTM D2369.

Table 3 Analysis of Sealer-Primer by ASTM D6886 and analysis of same paint by modified D6886 using both direct and static headspace analysis

Analyte	THF, Direct	Water, Direct	Water, Headspace	Contribution to Coating VOC, Direct Methods
Ethylene glycol	2.63%	2.81%	2.73%	73g - 77g
Propylene glycol	0.36%	0.41%	0.39%	10g - 11g
AMP-95	ND	0.06%	ND	1g
Texanol	1.95%	2.20%	2.16%	54g - 60g
Surfynol	0.04%	0.05%	0.05%	1g
Total	4.98%	5.53%	5.33%	138g - 150g

% Texanol lost during D2369 volatiles determination	90.4%
Calculated water, wt %	40.2%
REPORTED VALUE, Coating VOC	142

#### D. Initial Studies with Two Component Coatings

In order to assess the possibility of using static headspace GC as a means for analyzing two-component coatings for VOC content, two coatings which are representatives of this class of coatings were analyzed. Both a low temperature cure (150°C) glycidyl methacrylate powder coating and a melamine-cure (150°C) solventborne automotive primer were studied. While these two coatings are not examples of possible architectural coatings under study in this project, the methods developed in their analyses should apply to two-component coatings of virtually any type.

In the static headspace method a small portion of a two-component mixture is placed in a 22mL headspace vial and sealed with a crimp cap. The volatile components are thus sealed into the headspace vial. To analyze the volatile components in the vial, the vial is heated to a suitable

temperature (110°C if doing an EPA Method 24 total organic volatiles determination or the specified cure temperature for a specific powder coating or melamine-cure coating), and the volatiles are transferred by the headspace system to the GC capillary column for analysis by either flame ionization or mass spectrometry. Chromatograms of the two coatings tested appear in Figures 6 and 7.

Figure 6. Static Headspace Chromatogram of a Glycidyl Methacrylate Powder Coating Cured at 150°C.

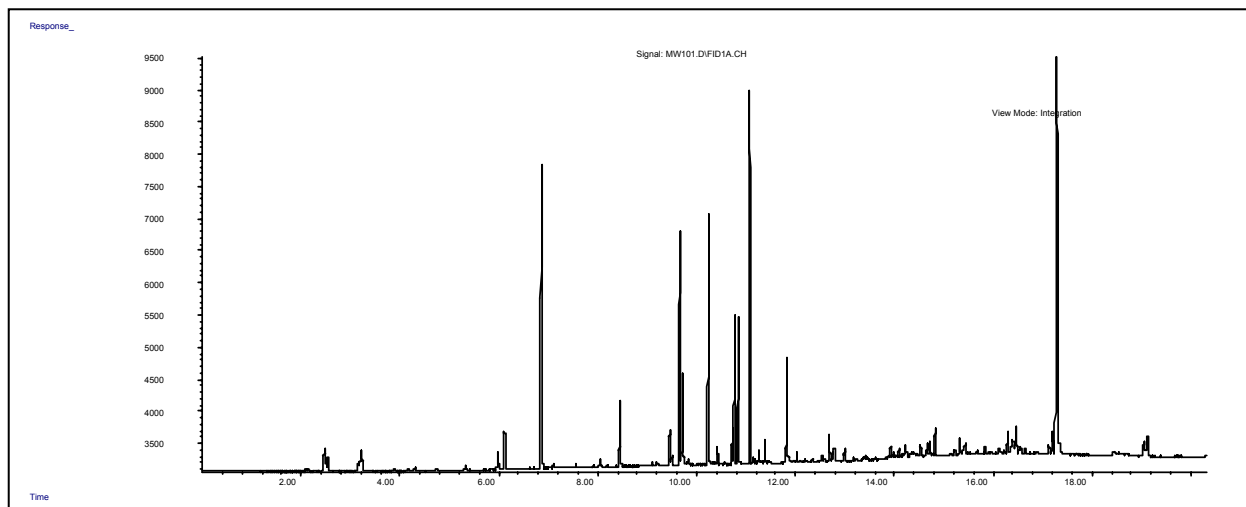
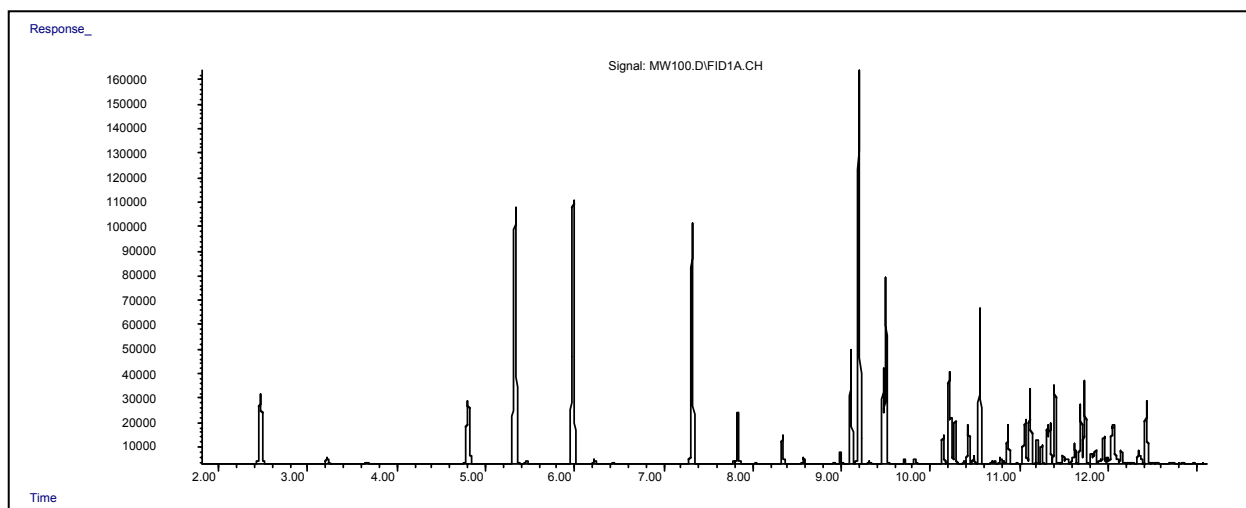


Figure 7. Static Headspace Chromatogram of a Melamine-Cure Solventborne Automotive Primer Cured at 150°C



## Discussion

Nearly all of the peaks in the chromatograms shown in Figures 6 and 7 have been identified. Identification is by mass spectrometry or FID retention time comparison with known compounds. Addition of a suitable internal standard makes it possible to quantify all of the components. Since the two coatings illustrated here are essentially two-component systems (a powder coating is a mixture of two or more reactive solids which cure when heated above the melting point; a melamine-cure system is a mixture of two reactive liquids dissolved in a suitable solvent and cures when subjected to a designated higher temperature), this technique should be suitable for any two-component system including architectural industrial maintenance coatings. Efforts are presently underway to use static headspace analysis to analyze several two component industrial maintenance coatings obtained from our NPCA/SCAQMD Rule 1113 VOC assessment study and we anticipate a specific method for two component architectural coatings and detailed results will be available for these coatings by the next reporting period.

## **II. Future work**

We should complete our work on Phase I and will continue work on methods development during the next period.

## **III. Overall progress of project.**

Project is on time and on budget.